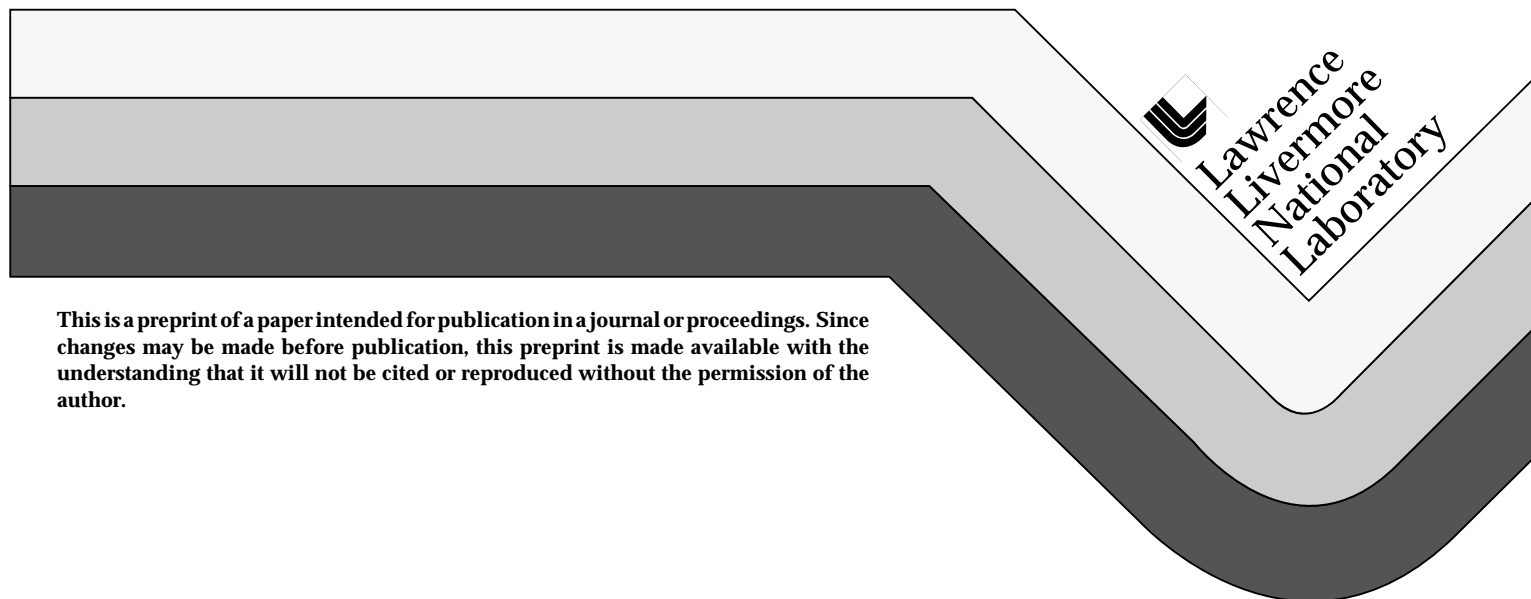


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# **$^{129}\text{I}$ Interlaboratory Comparison**

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## **Abstract**

An interlaboratory comparison exercise for  $^{129}\text{I}$  has been organized and conducted. A total of seven laboratories participated in the exercise to either a full or limited extent. In the comparison, a suite of 11 samples was used. This suite of standards contained both synthetic 'standard type' materials (i.e., AgI) and environmental materials. The isotopic  $^{129}\text{I}/^{127}\text{I}$  ratio of the samples varied from  $10^{-8}$  to  $10^{-14}$ . Preliminary results of the comparison are presented.

We wish to thank the U.S. Department of Energy, International Safeguards Division, NN-44 for their support of this project.

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## Introduction

In April 1993, at an IAEA consultant's meeting in Vienna, several technical issues relating to environmental monitoring, sampling, and analyses for the detection of undeclared nuclear activities were raised and discussed. In particular, Accelerator Mass Spectrometry (AMS) was identified as an important high sensitivity analysis technique for the detection of  $^{14}\text{C}$  and  $^{129}\text{I}$ . Detection of  $^{14}\text{C}$  using AMS is a well established technique used in wide range of scientific applications. Some thirty laboratories worldwide have established a  $^{14}\text{C}$  AMS analysis capability. Through the efforts of the radiocarbon dating community, appropriate standards, blanks, and analysis protocols have been determined and several round robin exercises have been performed. With established sample handling and preparation procedures, the precision and accuracy of a  $^{14}\text{C}$  AMS analysis is seldom in doubt. Unfortunately, this degree of intercomparison has not yet been achieved for  $^{129}\text{I}$  AMS analysis. A very limited number of laboratories have established analysis techniques for  $^{129}\text{I}$  AMS, and typically, each laboratory has its own independent standards and blanks by which abundance concentrations are determined.

Because of these unresolved questions about  $^{129}\text{I}$  AMS measurements, LLNL proposed and was funded by the U.S. Department of Energy to sponsor an  $^{129}\text{I}$  round robin exercise on behalf of the IAEA. From the IAEA's point of view, the purpose of the  $^{129}\text{I}$  round robin exercise was to assess the suitability, effectiveness and costs of  $^{129}\text{I}$  AMS measurements for possible safeguards use. For the  $^{129}\text{I}$  round robin exercise to be of maximum usefulness to the IAEA, it was important that the exercise contain environmental material of the type that the IAEA would expect to acquire on a typical field trial or inspection. As described by the IAEA, types of environmental samples that might be acquired on a field trial include swipes, filters, soils, grasses, lichens or moss, deciduous leaves, tree bark, pine needles, sediments, water, and water biota (e.g., algae, mussels, plants).

Eleven laboratories were invited to take part in the exercise and, at the time of writing, results, although not complete, have been received from seven laboratories. A list of the laboratories that participated in the exercise is listed in the acknowledgments.

## Samples

In February of 1995, LLNL prepared a suite of 11  $^{129}\text{I}$  proficiency samples and shipped those samples to the participating laboratories. The sample list was developed from discussions with the IAEA and contained both synthetic 'standard type' materials (e.g., AgI) and environmental materials of the type that the IAEA would expect to acquire on a typical field trial or inspection. The specific samples were:

- Sample #1:** Prepared AgI.  $^{129}\text{I}/^{127}\text{I}$  ratio approximately  $90308 \times 10^{-15}$ .
- Sample #2:** Prepared AgI.  $^{129}\text{I}/^{127}\text{I}$  ratio approximately  $45474 \times 10^{-15}$ .
- Sample #3:** Prepared AgI.  $^{129}\text{I}/^{127}\text{I}$  ratio approximately  $21729 \times 10^{-15}$ .
- Sample #4:** Prepared AgI.  $^{129}\text{I}/^{127}\text{I}$  ratio approximately  $4922 \times 10^{-15}$ .
- Sample #5:** Water sample.  $^{129}\text{I}/^{127}\text{I}$  ratio unknown but less than  $10^{-10}$ .
- Sample #6:** Spiked swipe. A Whatman filter paper spiked with  $^{129}\text{I}$ .
- Sample #7:** Pine needles.  $^{129}\text{I}/^{127}\text{I}$  ratio unknown but less than  $10^{-10}$ .
- Sample #8:** Maple leaves.  $^{129}\text{I}/^{127}\text{I}$  ratio unknown but less than  $10^{-8}$ .
- Sample #9:** Dried sea weed.  $^{129}\text{I}/^{127}\text{I}$  ratio unknown but less than  $10^{-8}$ .
- Sample #10:** Soil.  $^{129}\text{I}/^{127}\text{I}$  ratio unknown but less than  $10^{-10}$ .
- Sample #11:** Woodward Iodine.  $^{129}\text{I}/^{127}\text{I}$  ratio approximately  $50 \times 10^{-15}$ .

As can be seen, the isotopic  $^{129}\text{I}/^{127}\text{I}$  ratio of the samples varied from  $10^{-8}$  to  $10^{-14}$ .

The first three AgI samples had  $^{129}\text{I}/^{127}\text{I}$  ratios that are comfortably measured by the AMS technique. These three samples should provide some statistically meaningful intercomparison of the AMS technique at the various participating laboratories. The fourth AgI sample had an  $^{129}\text{I}/^{127}\text{I}$  ratio much lower than the first three AgI samples and provided a 'low-level' intercomparison sample. The Woodward Iodine sample was included to help in the determination of backgrounds. All prepared AgI samples were precipitated from a bulk solution that had been derived by successive dilution's of a NIST standard material. The  $^{129}\text{I}/^{127}\text{I}$  ratio of the original NIST standard material was 0.4091.

The water sample was created using de-ionized and purified water. Iodine was added to this water in the form of iodide and stabilized in a basic solution using sodium bisulfite. Iodine concentration for this sample was approximately 250  $\mu\text{g I/g of H}_2\text{O}$ .

The remaining five samples on the list were included to represent environmental samples that the IAEA would typically collect. The swipe sample was a Whatman filter paper spiked with a known amount of  $^{129}\text{I}$ . The pine needle and soil samples were collected locally to LLNL and have  $^{129}\text{I}/^{127}\text{I}$  ratios such that the high sensitivity of the AMS technique is truly required to obtain isotopic abundance's. The seaweed and maple leaf samples were obtained external to the LLNL area and had sufficiently high  $^{129}\text{I}/^{127}\text{I}$  ratios that they could be measured by both thermal emission mass spectrometry and AMS. The seaweed, maple leaf, pine needle, and soil samples were all small aliquots of a much larger supply of sample material that had been blended and mixed. All samples were prepared identically, at the same time, and under the same conditions.

It is also important to note that the environmental samples that are included in the  $^{129}\text{I}$  round robin exercise were never intended to become environmental 'standards'. LLNL was never tasked, nor does LLNL have the personnel or financial resources, to develop 'NIST type' environmental  $^{129}\text{I}$  AMS standards. Our main intent with the chosen set of environmental samples was to help the IAEA determine to what level can one expect agreement between results obtained from different  $^{129}\text{I}$  AMS laboratories.

## **Intercomparison Procedure**

Samples were distributed to all laboratories that expressed a willingness to take part in the  $^{129}\text{I}$  round robin exercise. The only information given to the participating laboratories regarding  $^{129}\text{I}/^{127}\text{I}$  ratios of the individual samples was an approximate guide to the upper limit of the expected  $^{129}\text{I}/^{127}\text{I}$  ratio. Sufficient sample material was given to each laboratory such that several repeat measurements of each sample could be performed if necessary. Laboratories were asked to report the results for the AgI samples (samples 1,2,3, and 4) and the Woodward Iodine sample (sample 11) as ratios (i.e., number of  $^{129}\text{I}$  atoms per number of  $^{127}\text{I}$  atoms). For the water, swipe, and

other environmental samples (samples 5,6,7,8,9, and 10), laboratories were asked to report results as concentrations (i.e., the number of  $^{129}\text{I}$  atoms per gram of sample).

## Results

Results of the  $^{129}\text{I}$  round robin exercise are shown in Table 1. In order to preserve the anonymity promised to the participating laboratories, and the preliminary nature of some of the measurements, individual laboratories are identified only by code.

## Conclusions

Because of unresolved questions about  $^{129}\text{I}$  AMS measurements, an interlaboratory comparison exercise for  $^{129}\text{I}$  has been organized and conducted. The primary purpose of this  $^{129}\text{I}$  round robin exercise was to assess the suitability, effectiveness and costs of  $^{129}\text{I}$  AMS measurements for possible IAEA safeguards use. At the time of this writing, results of the exercise were preliminary. However, if one ignores one 'outlying' data set, one can see from the data collected so far that  $^{129}\text{I}$  AMS measurements obtained at differing laboratories are in agreement. The one laboratory with outlying values will be encouraged to recheck their work.

In conjunction with the 7th International Conference on Accelerator Mass Spectrometry, LLNL hosted a one day pre-conference workshop that concentrated on the application of the  $^{129}\text{I}$  AMS technique. Most of the participants in the  $^{129}\text{I}$  round-robin exercise were present at the workshop. A major part of this workshop was the discussion of the results from the present  $^{129}\text{I}$  round-robin exercise, the need for the establishment of an international set of standards and blanks for  $^{129}\text{I}$  AMS, sample preparation methods, and the possible need for a second round of the  $^{129}\text{I}$  round-robin exercise.

## Acknowledgments

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Switzerland (Hans-Arno Synal), Isotrace Laboratory, Toronto, Ontario, Canada (Linas Kilius), Prime Laboratory, West Lafayette, Indiana, USA (Pankaj Sharma), and Racah Institute of Physics, Hebrew University, Jerusalem, Israel (Michael Paul). We also wish to thank the U.S. Department of Energy, International Safeguards Division, NN-44 for their support of this project.



**Table 1**  
**Results of the  $^{129}\text{I}$  Round Robin Exercise**  
(Results current as of 4/19/96 and are subject to change)

Laboratory Code	Sample #1 AgI $^{129}\text{I}/^{127}\text{I}$ Ratio	Sample #2 AgI $^{129}\text{I}/^{127}\text{I}$ Ratio	Sample #3 AgI $^{129}\text{I}/^{127}\text{I}$ Ratio	Sample #4 AgI $^{129}\text{I}/^{127}\text{I}$ Ratio	Sample #5 Water Sample $^{129}\text{I}$ atoms/gram
B	8.41E-11 ± 2.30E-12	4.28E-11 ± 8.00E-13	2.13E-11 ± 4.00E-13	4.76E-12 ± 8.00E-14	
W	9.01E-11 ± 4.51E-12	4.78E-11 ± 2.39E-12	2.19E-11 ± 1.10E-12	4.90E-12 ± 2.45E-13	1.22E+07 ± 6.10E+05
G	5.00E-11 ± 8.00E-12	3.30E-11 ± 7.00E-13			
K	8.38E-11 ± 2.10E-12	4.22E-11 ± 1.03E-12	2.03E-11 ± 5.40E-13	4.85E-12 ± 1.20E-13	1.83E+07 ± 4.80E+05
M	8.39E-11 ± 9.70E-12	4.35E-11 ± 6.54E-12	2.09E-11 ± 2.28E-12	5.28E-12 ± 1.93E-13	1.12E+07 ± 4.61E+05
Q	8.66E-11 ± 1.50E-12	4.32E-11 ± 7.00E-13	2.07E-11 ± 3.00E-13	5.00E-12 ± 7.00E-14	
Laboratory Code	Sample #6 Spiked Swipe $^{129}\text{I}$ atoms/gram	Sample #7 Pine Needles $^{129}\text{I}$ atoms/gram	Sample #8 Maple Leaves $^{129}\text{I}$ atoms/gram	Sample #9 Sea Weed $^{129}\text{I}$ atoms/gram	Sample #10 Soil $^{129}\text{I}$ atoms/gram
Z			5.89E+07 ± 4.70E+06		
W	1.97E+08 ± 1.38E+07	1.62E+07 ± 2.43E+06	3.10E+07 ± 4.65E+06	1.78E+09 ± 1.25E+08	1.16E+07 ± 3.48E+06
M		6.80E+08 ± 5.18E+07	5.21E+09 ± 1.92E+08	3.32E+09 ± 1.29E+08	2.46E+08 ± 1.38E+07
Q					
Laboratory Code	Sample #11 Woodward Iodine $^{129}\text{I}/^{127}\text{I}$ Ratio				
W	8.00E-14 ± 2.00E-14				
K	9.00E-14 ± 3.00E-14				
Q	5.30E-14 ± 1.60E-14				